

Formation Mechanism of HCN and NH₃ during Indole Pyrolysis: A theoretical DFT study

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Abstract: Coal is a major contributor to the global emission of nitrogen oxides. The NO_x formation during coal utilisation typically derives from thermal decomposition of N-containing compounds pyrrole, which usually combines with an aromatic ring in the form of indole. NH₃ and HCN are common precursors of NO_x from the decomposition of N-containing compounds. In this study, possible pathways of indole pyrolysis to form HCN and NH₃ are investigated using the density functional theory (DFT) method. Calculation results indicate that indole pyrolysis has two type of possible initial reactions, which are internal hydrogen transfer and hydrogen homolysis reaction, respectively. The initial reaction mode of indole has a great impact on the subsequent pyrolysis pathway. Additionally, it is shown that indole can produce two nitrogen-containing products, i.e. HCN and NH₃. Five pathways will result in the formation of HCN (path-1, path-3, path-a, path-b, path-c), and another two pathways will lead to the NH₃ (path-2, path-4). Furthermore, among all the reaction mechanisms of indole pyrolysis, the path-1 is the optimal reaction pathway. During which, indole is converted to a diradical intermediate, then the intermediate undergoes a synergy ring-opening transition state to form a new intermediate. Afterwards, the new intermediate decomposes into CN by homolysis of the C-C bond.

Keywords: NO_x; indole pyrolysis; NH₃; HCN; DFT

1. Introduction

Coal usage is the main sources of nitrogen oxide (NO , NO_2 , N_2O) in the atmosphere. Nitrogen oxide is not only the main precursor of acid rain formation, but also has a severe greenhouse effect which is 260 times that of CO_2 [1]. Nitrogen species exist in coal in many forms. The chemical structure of coal is inlaid with organic macromolecules, mainly composed of aromatic rings, bond bridges and functional groups (Wiser model [2], Shinn model[3]). As a matter of fact, the Wiser model along with “structural alternative” carbon skeletal representations, had an increasing scale, representing the rank transition from 76% C to 90% C (wt % basis) [2]. The Shinn model was created at a larger scale, in which three relatively small unconnected molecular entities were held within a larger molecule[3].

Three types of N-containing compounds exist in coal: pyrrole-N, pyridine-N, and quaternary-N. The dominant nitrogen source in coal is the pyrrole type, which accounts for 50–80 wt.% of total nitrogen [4]. Pyrrole is not presented in coal alone[3], usually combines with an aromatic ring in the form of carbazole, indole or naphthazole[5]. Consequently, merely studying the mechanism of pyrrole pyrolysis[6] is not comprehensive to reveal the formation mechanism of NO_x pollutant precursors. In fact, nitrogen has been found in coal and coal tar in the form of indole[7, 8]. Moreover, Yamamoto et al.[9] have extracted the indole and its derivatives from coal tar as platform compounds. It should be noted that indole has a stable structure composed by benzene and pyrrole. Furthermore, indole is difficult to decompose during the pyrolysis process of coal. Therefore, studying the indole pyrolysis reaction mechanism is crucial for understanding the formation and control of NO_x .

The research on the mechanism of indole pyrolysis is mainly through the experimental method. Corval et al.[10] investigated the mechanism of indole pyrolysis to form HCN by carbon labelling. The results suggested that indole decomposition is a complex isomerization process, which provides evidence for the mechanisms of HCN elimination. Moreover, Ren et al.[11] reported that the coal-N (nitrogen in coal) model compound indole can form HCN when the reaction reached the temperature threshold. In addition, Laskin et al.[12] studied the mechanism of indole pyrolysis by combining experimental and molecular dynamics methods, studies have described the pyrolysis mechanism of indole. However, the experimental and molecular dynamics studies follow the macro-Newtonian mechanics, so the reaction mechanism cannot be clear at the quantum level. With the advance of computational density theory, progresses have been made in the mechanism study of indole pyrolysis. Zhou et al.[13] explored the pyrolysis mechanism of

indole by density functional theory, focusing on the mechanism of indole open loop reaction. It is believed that the structure of benzene is more stable than that of pyrrole during the pyrolysis reaction of indole[14]. As a result, the indole pyrolysis reaction begins from the pyrrole ring opening reaction.

It has been identified that HCN and NH₃, generated during coal utilization under high temperature, are the main precursors of NO_x[15, 16]. Hence, the thermal decomposition of N-containing model compounds to NH₃ and HCN is important for understanding NO_x formation. However, limited studies have been reported focusing on the formation mechanism of NO_x pollutant precursor by coal-N model compound indole pyrolysis. Therefore, in this study, the density functional theory (DFT) method was applied to investigate the detailed pyrolysis mechanism of indole to HCN and NH₃, which may help with the development of coal pyrolysis/combustion technologies for NO_x control.

2. Methodology

All calculations were carried out using the Gaussian 09 program[17]. The equilibrium geometries of the reactants, intermediates, transition states, and products were optimized by the density functional theory (DFT) computational method and employing B3LYP/6-31G(d, p) basis set. The Becke's three-parameter hybrid functional combined with the Lee, Yang, and Parr correlation functional B3LYP[18] run with the 6-31G(d, p) basis set[19] has been successfully applied to investigate the pyrolysis mechanism of pyrrole model compounds[20, 21]. In this work, the optimized structures of the reactants, intermediates, transition states, and products were further evaluated by frequency analysis, adopting the same method and basis set as the structural optimization calculations. The results of a frequency analysis were used to verify the stationary points to be minimal or first-order saddle points and to obtain their thermodynamic parameters. Intrinsic reaction coordinate (IRC) calculations were further performed to ensure the corresponding minimal and first-order saddle point on the same potential energy surface. Enthalpies were used for the discussion on energetics, under the standard conditions of 298.15 K and 1 atm[22].

Indole is a heterocyclic organic compound with the formula C₈H₇N. The optimized molecular structure of indole is shown in Figure 1. All carbon atoms are marked with numbers for convenient expression.

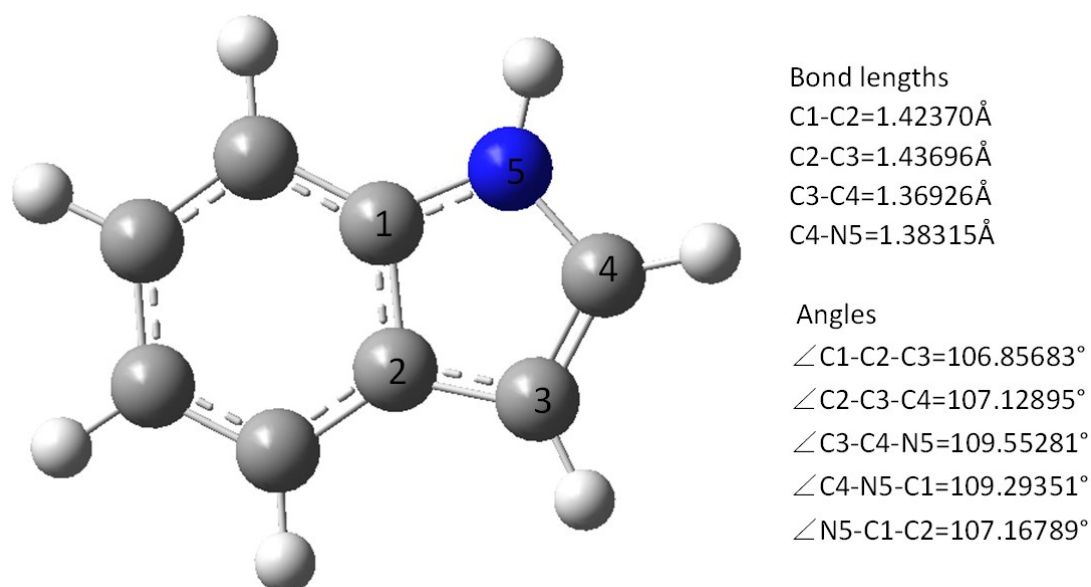


Figure 1. The molecular structure information of indole. The blue spheres represent nitrogen atoms; the grey spheres represent carbon atoms, and the white spheres represent hydrogen atoms.

3. Results and Discussion

Early studies have mentioned[12, 23, 24] that the initial reaction type of indole thermal decomposition can be divided into two types. One is indole internal hydrogen transfer reaction, the other is the homolysis reaction on the indole ring. The hydrogen transfer reaction can destroy the stability of the pyrrole ring in indole to facilitate subsequent reactions. There are eight possible ways for this type of reaction, which are the hydrogen on C₅ transferred to C₁, the hydrogen on C₃ transferred to C₁, the hydrogen on N transferred to C₁, the hydrogen on N transferred to C₇, the hydrogen on C₇ transferred to N, the hydrogen on C₇ transferred to C₈, the hydrogen on C₈ transferred to C₇, the hydrogen on C₈ transferred to C₂. Among all these reactions, there are four possibilities for the subsequent path generating product to be HCN or NH₃, as shown in Figure 2. The four reactions are the hydrogen on C₇ transferred to C₈ (reaction-1), the hydrogen on C₈ transferred to C₇ (reaction-2), the hydrogen on N transferred to C₁ (reaction-3), and the hydrogen on N transferred to C₇ (reaction-4).

The homolysis reaction of indole mainly includes N-H bond homolysis and C-H bond homolysis. There are three possibilities to finally generate HCN or NH₃, namely, reaction-

a (the homolytic cleavage of N-H bond), reaction-b (the homolytic cleavage of C₇-H bond) and reaction-c (the homolytic cleavage of C₈-H bond).

3.1 The comparison of different initial reactions

Firstly, hydrogen transfer is used as an initial mode to induce indole thermal decomposition. As shown in Figure 2, the reaction-1 activation energy is 260.9 kJ/mol; the activation energy of the reaction from indole to indole-2 is 302.76 kJ/mol; the activation energy of the internal hydrogen transfer process indole→indole-3 is 226.92 kJ/mol; the activation energy from indole to indole-4 is 367.14 kJ/mol.

Secondly, the homolytic cleavage of C-H or N-H bond serves as an initial reaction, which can destroy the stability of indole structure, and then trigger subsequent dissociation. As shown in Figure 2, the homolytic dissociation enthalpy of N-H bond is calculated to be 372.95 kJ/mol. In the reaction of indole→indole-b, the homolytic cleavage of C₇-H bond is considerably less favourable, with an activation energy of 495.21 kJ/mol.

The reaction process indole→indole-c at site C₈ is energetically similar to reaction-b from indole to indole-b, with an activation energy of 497.77 kJ/mol. From the above calculated results, it can be concluded that the activation energies of homolysis reactions are generally higher than the activation energies of internal hydrogen transfer reactions.

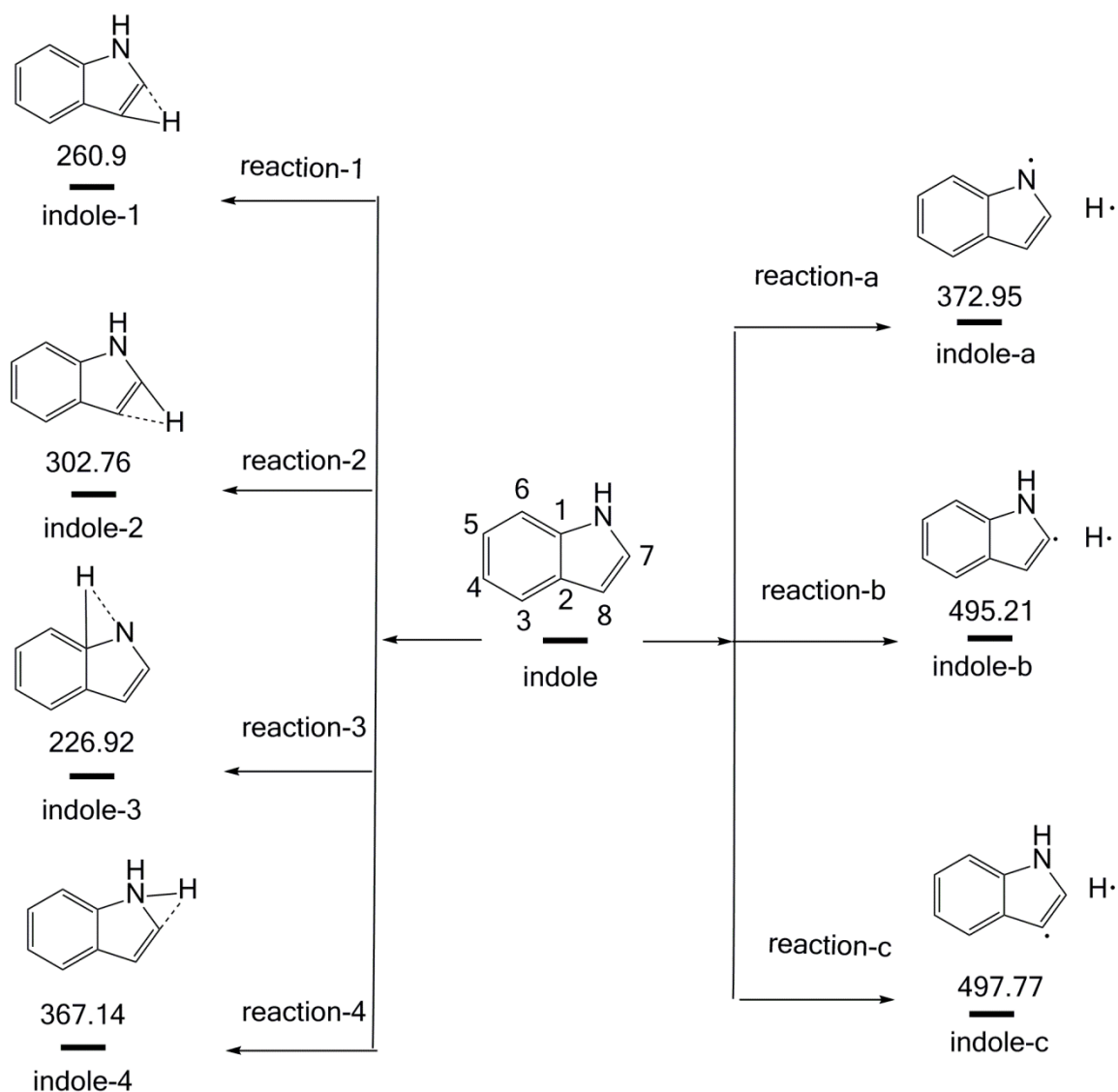


Figure 2. Initial interaction and pyrolysis mechanism of indole. The numerical values are energies in kJ/mol.

3.2 Reaction pathways for generating HCN or NH₃ by internal hydrogen transfer reactions of initial indole pyrolysis

Based on the internal hydrogen transfer reaction reaction-1, reaction-2, reaction-3 and reaction-4, four possible pathways (path-1, path-2, path-3, path-4) might occur and can be classified into two categories according to their products (NH₃ or HCN). NH₃ is produced through path-1 and path-3, as shown in Figure 3 and Figure 5, respectively, while in Figures 4 and 6, path-2 and path-4 generate HCN.

3.2.1 path-1

For path-1 in Figure 3, indole is converted to the diradical intermediate in-1-1m, via an internal hydrogen transfer transition state in-1-1t (the hydrogen transfers from C₇ to C₈), with an activation energy of 260.9 kJ/mol. Then the intermediate in-1-1m undergoes a synergy ring-opening transition state in-1-2t to form intermediate in-1-2m. This reaction requires an activation energy of 429.36 kJ/mol. Afterwards, intermediate in-1-2m decomposes into radicals in-1-3m and CN by homolysis of the C-C bond, with a high activation energy of 484.71 kJ/mol. In fact, coal pyrolysis has been confirmed to involve radical reactions[25]. During the pyrolysis process, with the gradual heating, the internal network structure of the coal begins to undergo bond cleavage reactions at 350-400 °C , and the homolytic breaking of covalent bonds in the network structure can generate reactive free radicals(H radicals & CH₃ radicals, etc.). Moreover, the cracking of alkanes and aromatics in long chain reactions occurs by C-C and C-H bond homolysis, and C-H bond homolysis competitively forms H radicals[26-28]. The free radical CN easily combines with hydrogen radicals to form HCN. The relative energy of the final products in-1-3m and HCN is -48.79 kJ/mol. In path-1, the homolysis reaction in which the products are radicals of in-1-3m and CN is the determining step with an overall activation energy of 484.71 kJ/mol.

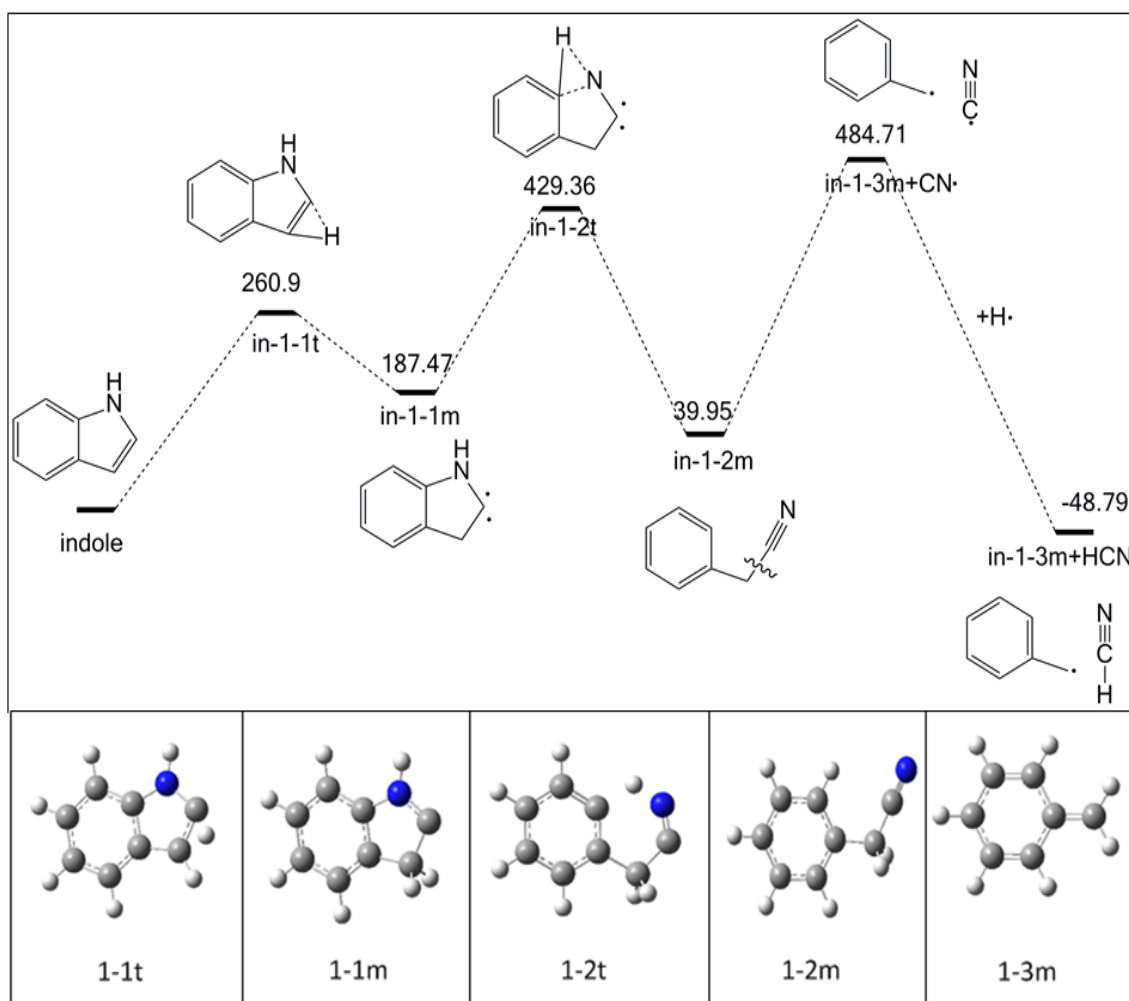


Figure 3. Pyrolytic reaction pathways based on path-1 to generate HCN. The numerical values are energies in kJ/mol.

3.2.2 path-2

As shown in Figure 4, indole undergoes a hydrogen transfer reaction (the hydrogen atom transfers from C₈ to C₇) through transition state in-2-1t to form the diradical intermediate in-2-1m, and needs to overcome an energy barrier of 302.76 kJ/mol. Then intermediate in-2-1m forms 2-ethynylaniline(in-2-2m) via a synergy ring-opening transition state in-2-2t with an activation energy of 360.19 kJ/mol. Finally, an activation energy of 598.23 kJ/mol is required to split intermediate in-2-2m through a homolysis reaction into the radicals in-2-3m and NH₂. Generally, the free radical NH₂ readily combines with H radicals to form NH₃. According to the calculation results, the rate-determining step is the reaction to

generate radicals in-2-3m and NH_2 , and the overall activation energy of path-2 is 598.23 kJ/mol.

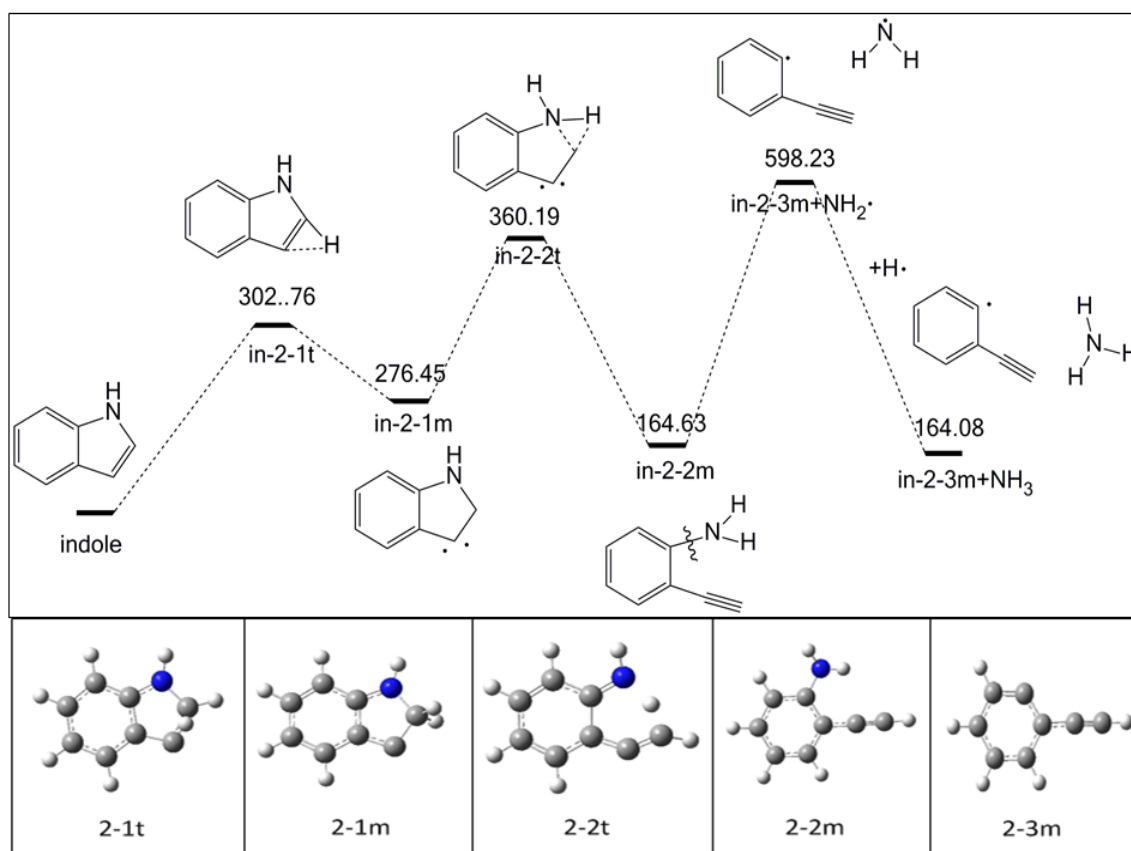


Figure 4. Pyrolytic reaction pathways based on path-2 to generate NH_3 . The numerical values are energies in kJ/mol.

3.2.3 path-3

In terms of path-3, as shown in Figure 5, the hydrogen transfer step occurs on the nitrogen atom and bonds the hydrogen atom to the adjacent carbon atom (C_1), converting indole to intermediate in-3-1m which loses the benzene ring structure. The reaction is carried out through a transition state of in-3-1t, and the activation energy of the reaction is 226.92 kJ/mol. Afterwards, intermediate in-3-1m undergoes a synergy ring-opening transition state in-3-2t to form a diradical intermediate in-3-2m, which needs to overcome an activation energy of 527.74 kJ/mol. Then the diradical intermediate in-3-2m decomposes into the radical products in-3-3m and CN by the homolysis of the C-N bond, with an activation energy of 484.71 kJ/mol. Finally, the free radical CN forms a covalent

bond with the hydrogen radical to obtain HCN. Additionally, the rate-determining step is the reaction that undergoes in-3-2t transition state, and the overall activation energy of path-3 is 527.74kJ/mol.

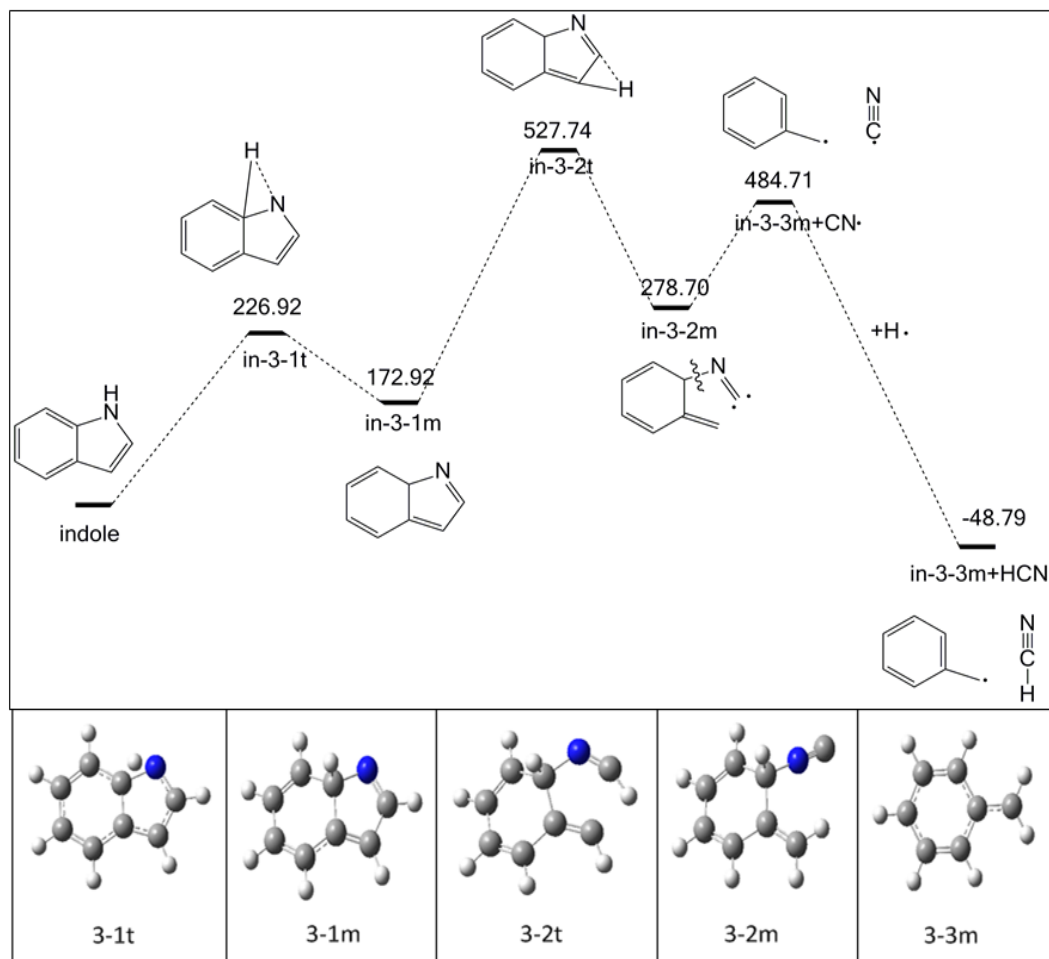


Figure 5. Pyrolytic reaction pathways based on path-3 to generate HCN. The numerical values are energies in kJ/mol.

3.2.4 path-4

In figure 6, indole in path-4 undergoes a hydrogen transfer synergistic ring opening reaction, and the hydrogen atom on C₇ is bonded to the adjacent nitrogen atom through the transition state in-4-1t to form a diradical intermediate in-4-1m, with an activation energy of 367.14 kJ/mol. Then the intermediate in-4-1m via a hydrogen transfer transition state in-4-2t to form intermediate in-4-2m (2-ethynylaniline) with an activation energy of 352.56 kJ/mol. Similar to path-2, the intermediate in-4-2m decomposes into radical products in-4-3m and NH₂ through a homolytic bond cleavage reaction, and a high

activation energy of 598.23 kJ/mol is required. The radical NH_2 then bonds with the hydrogen radical to form the target product NH_3 . The relative energy of the final products in-4-3m and NH_3 is 164.08 kJ/mol. The rate-determining step is the reaction to generate radicals in-4-3m and NH_2 , and the overall activation energy of 598.23 kJ/mol needs to be overcome in path-4.

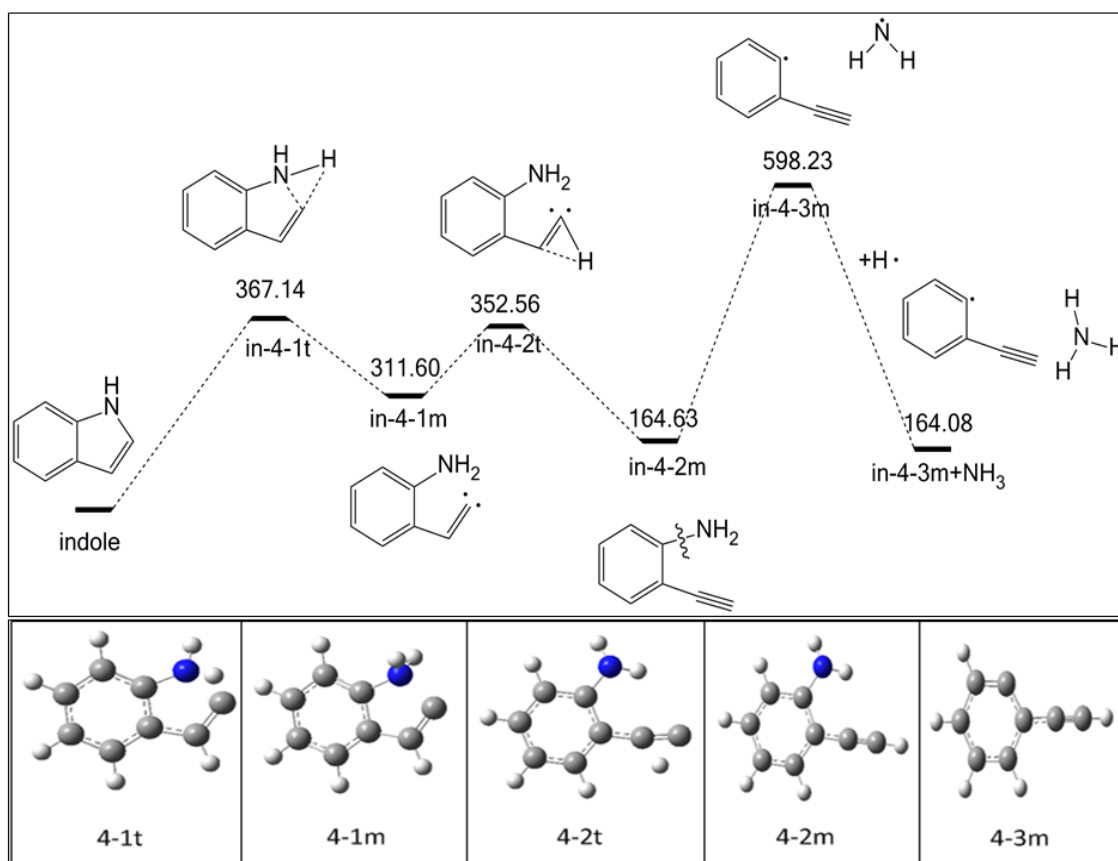


Figure 6. Pyrolytic reaction pathways based on path-4 to generate NH_3 . The numerical values are energies in kJ/mol.

According to above calculation results, indole undergoes different pathways path-1 and path-3 to form HCN. In path-1, the rate-determining step is the homolysis reaction that generates CN radicals with the overall activation energy of 484.71 kJ/mol. However, in path-3, the rate-determining step is the hydrogen transfer synergistic ring opening reaction requiring 537.74 kJ/mol. Clearly, compared with path-3, path-1 has an advantage in generating HCN.

For both path-2 and path-4, where the final products are NH_3 , their rate-determining steps are the $\text{C}_1\text{-N}$ bond homolytic cleavage reaction of 2-ethynylaniline which generates

free radicals NH_2 , so their overall activation energy is the same as 598.23 kJ/mol. Comparing the activation energies of each path, we can conclude that HCN is generally more likely to form than NH_3 when the first step of indole pyrolysis is hydrogen transfer.

3.3. Reaction pathways to generate HCN or NH_3 by reaction of initial indole pyrolysis

According to the possibility of that the homolysis reaction is the first step in indole pyrolysis, we chose three more active reaction sites (reaction-a, reaction-b and reaction-c in Fig.2). Based on these three active sites, we designed three reaction paths, path-a, path-b and path-c. Subsequently, the details of the discussion are presented separately.

3.3.1 path-a

In the first pathway (path-a), as shown in Figure 7, indole undergoes a homolysis reaction, that the hydrogen radical is split from the nitrogen atom on indole to generate a radical intermediate in-a with an activation energy of 372.95 kJ/mol. The intermediate in-a following transfers a hydrogen atom from C_7 to C_8 in the form of transition state in-a-1t, which needs an activation energy of 643.45 kJ/mol. After the hydrogen transfer reaction, two unpaired electrons are formed on the C_7 atom, and one of the unpaired electrons bonded with the unpaired electron on the nitrogen atom immediately to form the intermediate in-a-1m. Afterwards, the intermediate in-a-1m undergoes a $\text{C}_7\text{-C}_8$ bond homolysis transition state in-a-2t to form a triradical intermediate in-a-2m, and the reaction activation energy is 577.26 kJ/mol. Finally, the intermediate in-a-2m decomposes into products in-a-3m diradical and CN radical through a homolysis reaction with a significantly large activation energy of 947.83 kJ/mol. The radical CN easily combines with the hydrogen radical in the system to form HCN. Therefore, for path-a it is difficult to occur due to the relatively high energy of rate-determining step (947.83 kJ/mol).

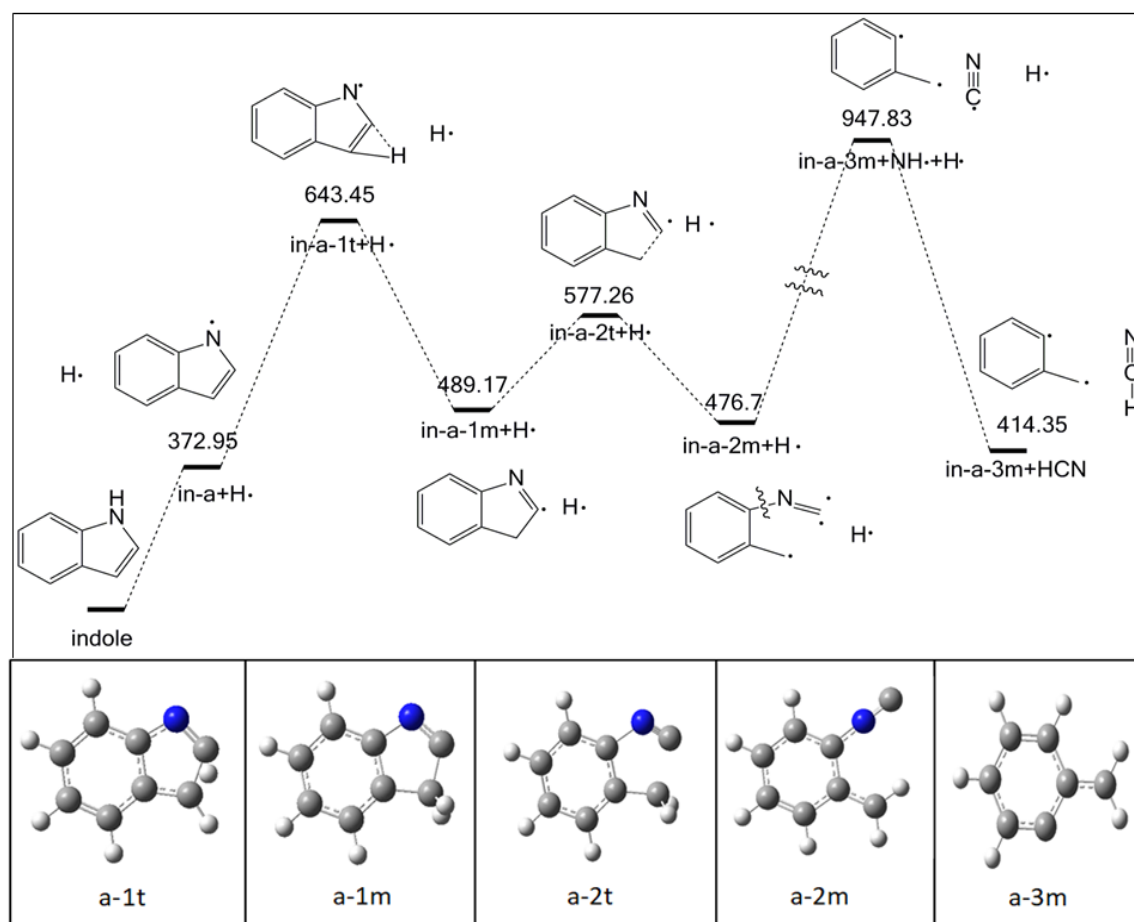


Figure 7. Pyrolytic reaction pathways based on path-a to generate HCN. The numerical values are energies in kJ/mol.

Figure 8 shows the reaction mechanism of path-b, as is seen in the reaction diagram indole undergoes C₇-H bond homolysis reaction to generate the radicals in-b and H with an activation energy of 459.21 kJ/mol. Then the intermediate in-b via hydrogen transfer transition state in-b-1t (the hydrogen on nitrogen atom is bonded to the adjacent carbon atom C₁) to form the intermediate in-b-1m, and the activation energy is 700.66 kJ/mol. Furthermore, the intermediate in-b-1m undergoes a transition state in-b-2t which is the homolytic cleavage of N-C₁ bond to generate a radical intermediate in-b-2m with a 651.36 kJ/mol activation energy. A homolysis reaction occurs on the intermediate in-b-2m to generate the radical CN and diradical in-b-3m. This process needs to overcome a high activation energy of 948.21 kJ/mol. Finally, the radical CN combines with the hydrogen radical in the system to form HCN. In a result, the reaction bearing the highest activation

energy barrier among all the reactions in path-b is the reaction to generate diradical in-b-3m. 3m.

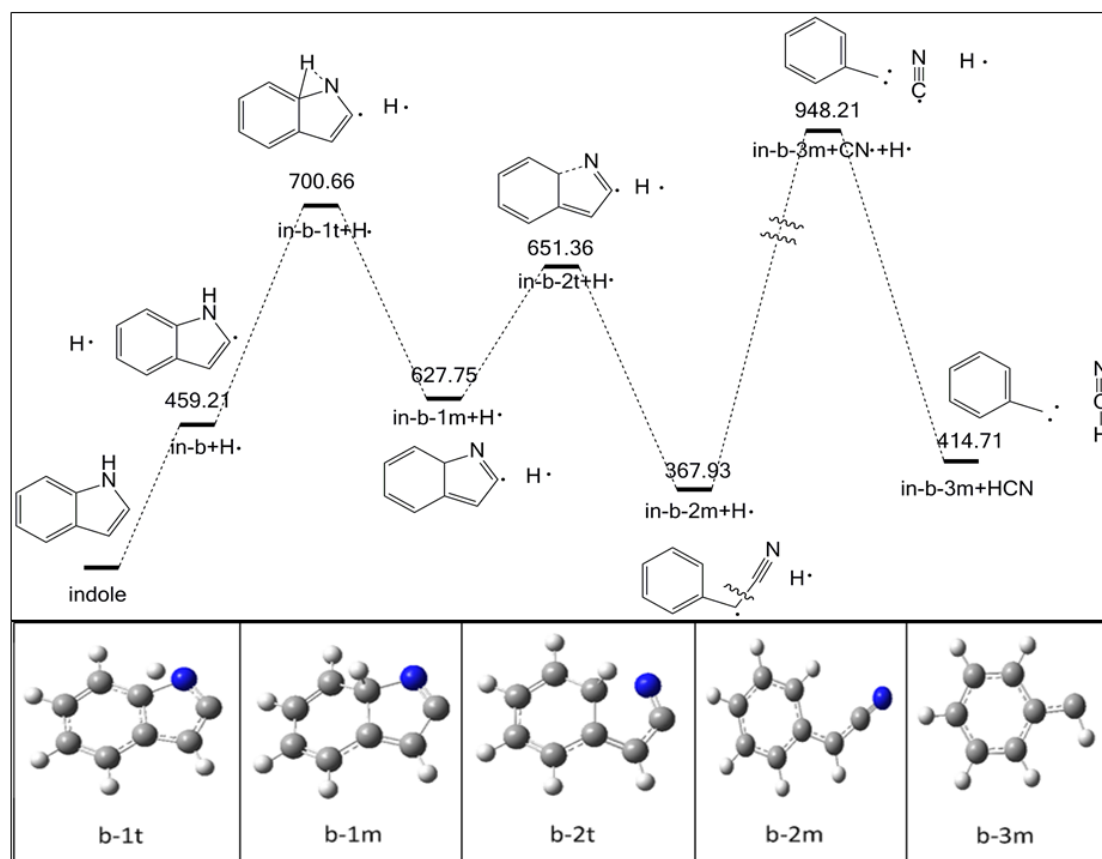


Figure 8. Pyrolytic reaction pathways based on path-b to generate HCN. The numerical values are energies in kJ/mol.

Path-c, as presented in Figure 9, is also initiated through a C₈-H bond homolysis reaction from indole to in-c with an activation energy of 497.77 kJ/mol. Then the intermediate in-c is converted into a radical intermediate in-c-1m by the internal hydrogen transfer transition state in-c-1t, to be specific, the hydrogen of the nitrogen atom is transferred to the adjacent C₁, and the activation energy is 716.8 kJ/mol. This intermediate in-c-1m undergoes another internal hydrogen transfer reaction (transfers a hydrogen atom from C₇ to C₈) to produce the intermediate in-c-2m with a significantly high activation energy of 981.89 kJ/mol. Afterwards, the intermediate in-c-2m via a C₁-N bond homolytic cleavage transition state in-c-3t to form intermediate in-c-3m, and the activation energy is 651.36 kJ/mol. Finally, intermediate in-c-3m decomposes into the radicals in-c-4m and CN, which needs to overcome a high activation energy of 948.21 kJ/mol and has the same products as path-b.

As a result, the rate-determining step in path-c is the reaction in which the hydrogen atom is transferred from C₇ to C₈ with an overall activation energy of 981.89 kJ/mol.

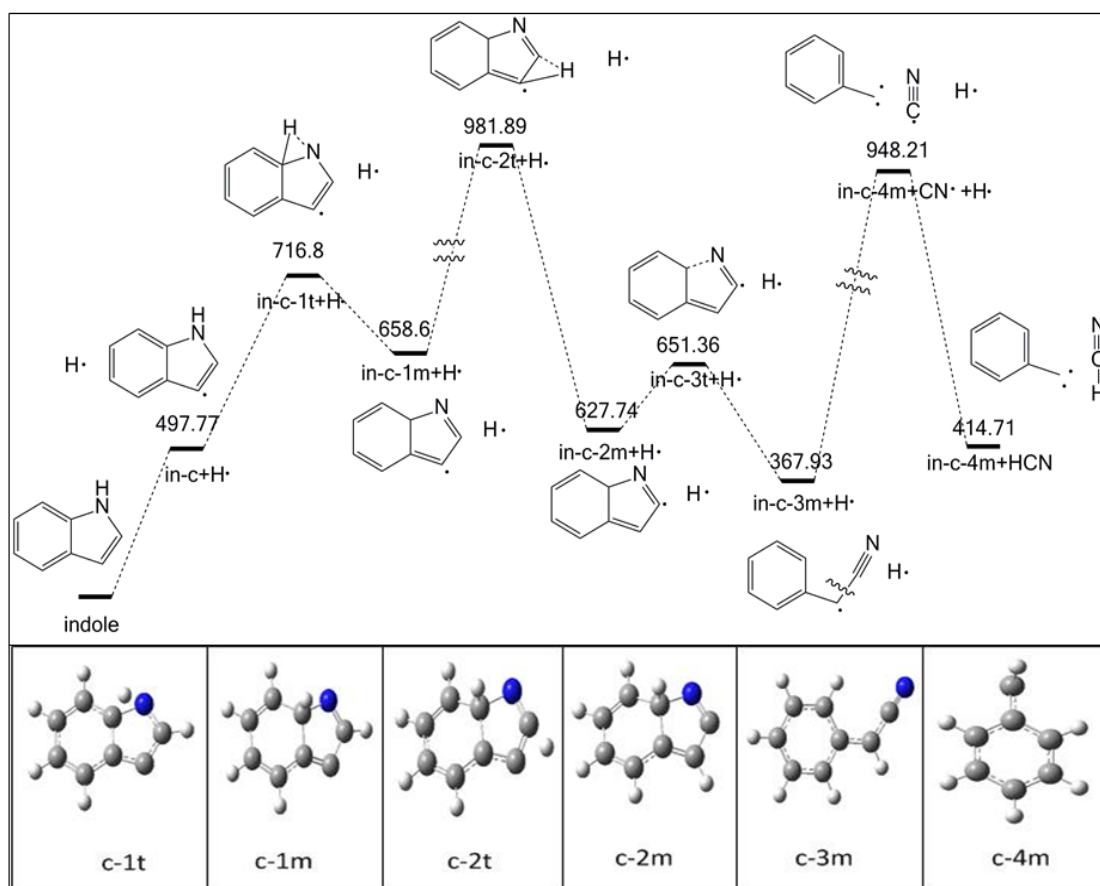


Figure 9. Pyrolytic reaction pathways based on path-c to generate HCN. The numerical values are energies in kJ/mol.

In summary, the initial reaction type of indole pyrolysis has significant influences on the formation of HCN or NH₃ as shown in Table 1. Two possible pathways (path-2, path-4) can generate the nitrogen-product NH₃ and five possible pathways (path-1, path-3, path-a, path-b and path-c) can generate the nitrogen-product HCN. In the case of by internal hydrogen transfer as the initial reaction, indole pyrolysis can generate NH₃ and HCN. The path-1 is the optimal reaction pathway with an activation energy of 484.71 kJ/mol, and the nitrogen-containing product is HCN. When the bond homolytic cleavage reaction on the indole is used to initiate the subsequent pyrolysis reaction, the nitrogenous product generated by indole pyrolysis can only be HCN, and the activation energies of the different pathways generally this condition are generally higher than the activation energies of the

former case. By comparing the calculated results, it is easier to initiate the subsequent reaction by internal hydrogen transfer, which is the dominant initial reaction mechanism for the formation of HCN and NH₃ by indole pyrolysis.

Table 1. Comparison of pathways and products from indole pyrolysis

No.	Pathways	Determining steps	The initial interaction types	Ea ^a (activation energy)	Product types
1	path-1	in-1-3m	synergy	484.71	HCN
2	path-2	in-2-3m	synergy	598.23	NH ₃
3	path-3	in-3-2t	synergy	537.74	HCN
4	path-4	in-4-3m	synergy	598.23	NH ₃
5	path-a	in-a-3m	homolysis	947.83	HCN
6	path-b	in-b-3m	homolysis	948. 21	HCN
7	path-c	in-c-3t	homolysis	981. 89	HCN

^a The units for relative energies are kJ/mol.

According to above calculation results, two conclusions can be drawn. Firstly, it is difficult to form HCN and NH₃ during the pyrolysis of indole, which is consistent with previous experimental studies. For instance, Jiang et al.[7] asserted that indole was mostly present in tar and coke in coal pyrolysis. Moreover, the structure was stable and it is more difficult to release nitrogen[29]. In fact, Wornat et al.[30] stated that N-heteroaromatic compounds were more thermally stable. Furthermore, Ledesma et al.[31] found that cyano aromatics in tar were stable N-containing structures at 1000 °C. Secondly, it is easier to generate HCN by indole pyrolysis than NH₃. This was agreed with experimental findings [32-34] such as Madeleine et al.[33] have compared H¹²CN and H¹³CN loss in two specifically labelled

indoles, providing evidence for HCN elimination from indole. Additionally, Ren et al.[34] believed that the cracking indole contributes to the higher HCN formation.

4. Conclusions

In this study, the formation mechanisms of HCN and NH₃ during indole pyrolysis are investigated by DFT calculation based on previous investigations on the experimental study of the nitrogen released from coal, and the research of the mechanism of the indole ring opening reaction. The specific conclusions are as follows:

1. The initial reaction mode of indole has a great impact on the subsequent pyrolysis pathways. The activation energy of indole pyrolysis with internal hydrogen transfer as the initial mode is generally lower than the hydrogen homolysis from indole.
2. Indole pyrolysis can produce two main nitrogen-containing products, HCN and NH₃. HCN is more likely to be generated than NH₃ by comparing all of calculated indole pyrolysis mechanisms.
3. In our calculations, the optimal reaction pathway for generating HCN is path-1. In this pathway, indole is converted to the diradical intermediate via a hydrogen transfers from C₇ to C₈, and then undergoes a synergy ring-opening reaction, finally, decomposes to get radical CN by homolysis of the C-C bond, with a high rate determining step activation energy of 484.71 kJ/mol.
4. For the path-2 and path-4 during which NH₃ is finally generated, their rate determining steps are the same, that is, the C₁-N bond of 2-ethynylaniline is homolytic cleaved to produce free radical NH₂, so their overall activation energy is 598.23. kJ / mol.

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